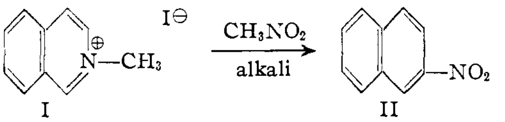
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reactions of Quinolinium Compounds with Nitromethane

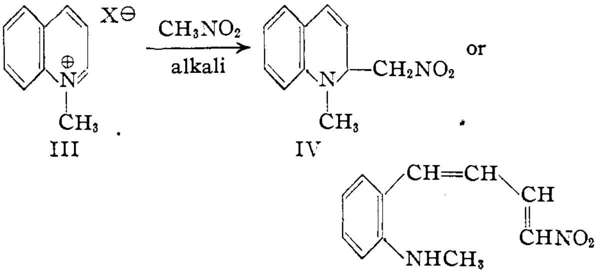
BY NELSON J. LEONARD, HARRY A. DEWALT, JR.,[1] AND GERHARD W. LEUBNER[2]

It has been established that 1-methyl-4-nitromethylenequinolane is produced from the condensation of 1-methylquinolinium iodide with nitromethane in the presence of base. Similar treatment of 1,2-dimethylquinolinium iodide yielded 1,2-dimethyl-4-nitromethylenequinolane, but 1,4-dimethylquinolinium iodide failed to yield an isomeric product. The structure of the product from 1-methylquinolinium iodide was proved by conversion to an amine, 1-methyl-4-aminomethyl-1,2,3,4-tetrahydroquinoline, which was identical with the compound obtained on reduction of 1-methyl-4-cyanoquinolinium iodide. In connection with the alternative possibility of reaction occurring at the 2-position, the N-methylation products of 2-aminomethyltetrahydroquinoline were synthesized and identified.

The unusual course of the reaction between 2-methylisoquinolinium iodide (I), nitromethane and base, resulting in the formation of 2-nitronaphthalene (II),[3,4] prompted an investigation of the results of a similar combination of reactants in the quinoline series. The condensation of nitromethane with quinoline methosulfate in the presence of base has been described in the patent literature,[5] but complete characterization of the condensation product was not provided, nor was there any indication whether reaction had occurred at the 2-position[6] or at the 4-position[7] of the quinoline nucleus. The product, in the form of brown-yellow needles, m.p. 210° (uncor.), with decomposition, obtained from III in about 70% yield was postulated by Kaufmann[5] to have either structure IV or V. In view of the same worker's synthesis of 4-cyanoquinoline[7] from quinoline methosulfate and potassium cyanide, it would seem unwise to exclude the possibility of structure VI as representing a $C_{11}H_{12}N_2O_2$ product obtainable from III using nitromethane and base.

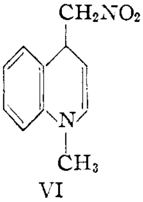


I II

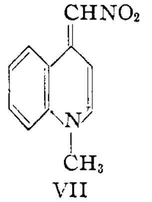


III IV V

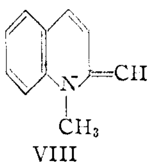
We have repeated the procedure of Kaufmann[5] and have applied a number of variations, some of which may help to elucidate the course of the reaction. Although we were unable to duplicate the yield previously claimed, we obtained a product, in the form of orange needles, m.p. 204° with decomposition, which is probably identical with that described by Kaufmann. Analysis of this compound, its hydrobromide and picrate, clearly indicated a composition of $C_{11}H_{10}N_2O_2$, suggestive of the dehydrogenated structure VII or VIII rather than the possible condensation precursor VI or IV. The orange color of the product also was more in keeping with the unsaturated species VII or VIII than with the dihydroquinoline species VI or IV, which would be expected to be colorless since 4-cyano-1-methylquinolane (as initially isolated)[7c] and 9-nitromethyl-10-methylacridan[8] are colorless.



VI



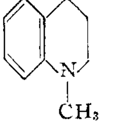
VII



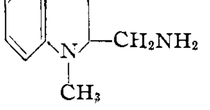
VIII

The occurrence of dehydrogenation following the combination of nitromethane with III was also indicated by the observation that the addition of nitrobenzene as an oxidizing agent improved the yield of $C_{11}H_{10}N_2O_2$ product. The optimum yield was obtained when equimolar quantities of nitromethane, 1-methylquinolinium iodide and sodium ethoxide were allowed to react in ethanol solution and nitrobenzene was added subsequently.

The decision between VII and VIII as representing the correct structure for the $C_{11}H_{10}N_2O_2$ product was made possible through the reduction of the aminonitro compound to the corresponding diamine. 1-Methyl-4-aminomethyl-1,2,3,4-tetrahydroquinoline (IX)[9] would be the expected reduction product if the initial substitution had occurred at the 4-position (VII), and 1-methyl-2-aminomethyl-1,2,3,4-tetrahydroquinoline (X),[9] if the initial substitution had occurred at the 2-position (VIII).



IX



X

---

[1] E. I. du Pont de Nemours and Company Fellow, 1949-1950; Eli Lilly and Company Fellow, 1948-1949.

[2] Eli Lilly and Company Fellow, 1946-1948.

[3] N. J. Leonard and G. W. Leubner, THIS JOURNAL, **71**, 3405 (1949).

[4] It has been possible to improve the yield of 2-nitronaphthalene realized in this isoquinoline-to-naphthalene conversion to at least 25%, and also, by varying the reaction conditions, to obtain instead an 82% yield of bis-[1-(2-methyl-1,2-dihydroisoquinolyl)]-nitromethane.

[5] A. Kaufmann, German Patent 250,154, July 15, 1912; *Frdl.*, **10**, 1317 (1910-1912).

[6] A. Reissert, *Ber.*, **38**, 1603 (1905).

[7] (a) A. Kaufmann, *ibid.*, **51**, 116 (1918); (b) A. Kaufmann and R. Widmer, *ibid.*, **44**, 2058 (1911); (c) A. Kaufmann and A. Albertini, *ibid.*, **42**, 3776 (1909).

[8] N. J. Leonard, G. W. Leubner and E. H. Burk, Jr., *J. Org. Chem.*, **15**, 979 (1950).

[9] To avoid unnecessary repetition, all compounds of this type will be referred to as tetrahydroquinolines rather than 1,2,3,4-tetrahydroquinolines.

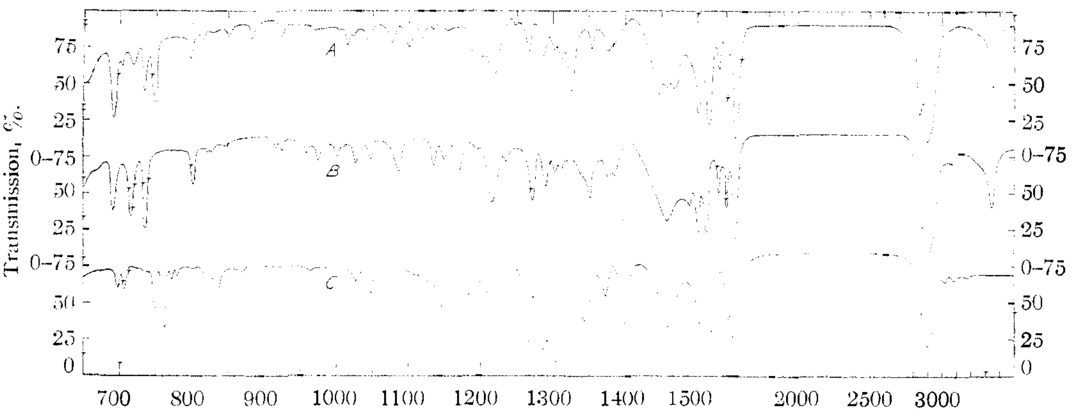
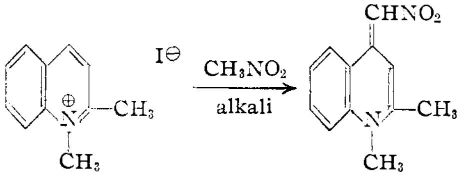


Fig. 1.—Infrared absorption spectra: A, 1-methyl-4-benzoylaminomethyltetrahydroquinoline; B, 1-methyl-2-benzoylaminomethyltetrahydroquinoline; C, 1-methyl-4-nitromethylenequinolane.

The hydrobromide of the $C_{11}H_{10}N_2O_2$ product was converted by low-pressure hydrogenation over Raney nickel in ethanol solution to a liquid diamine, $C_{11}H_{16}N_2$, which formed a monobenzoyl derivative, m.p. 143–144°. This benzoyl derivative was different from 1-methyl-2-benzoylaminomethyltetrahydroquinoline, m.p. 135–136°, prepared by a modification of the method of Rupe, Paltzer and Engel,[10] as clearly indicated by the non-identity of their melting points and infrared absorption spectra (Fig. 1, curves A and B). By contrast, the benzoyl derivative was established as identical with 1-methyl-4-benzoylaminomethyltetrahydroquinoline (m.p. 143–144°) by the superposability of their infrared absorption spectra curves (Fig. 1, curve A) and by the fact that admixture caused no depression in melting point. Authentic 1-methyl-4-benzoylaminomethyltetrahydroquinoline was provided by the hydrogenation of 1-methyl-4-cyanoquinolinium iodide in aqueous ethanol over platinum oxide to give 1-methyl-4-aminomethyltetrahydroquinoline (IX), followed by benzoylation. The properties of the two $C_{11}H_{16}N_2$ amines, as well as those of their benzoyl derivatives, were identical. The structure of the $C_{11}H_{10}N_2O_2$ product obtained by condensation of 1-methylquinolinium iodide with nitromethane in the presence of base was thereby established as 1-methyl-4-nitromethylenequinolane (VII). The product probably results from the combination of the anion derived from nitromethane with the cation derived from 1-methylquinolinium iodide and base to give the quinolane type VI, which immediately undergoes oxidation (for example, by nitrobenzene, nitromethane, alcoholic alkali or oxygen) to the methylenequinolane type VII.

The assignment of structure VII to the 1-methylquinolinium iodide product finds corroboration in the results obtained in extending the reaction to the homologs, 1-methyllepidinium iodide and 1-methylquinaldinium iodide. 1-Methyllepidinium iodide, which has a blocked 4-position, failed to give an isolable aminonitro product when treated with nitromethane and base, but 1-methylquinaldinium iodide (XI) yielded an orange $C_{12}H_{12}N_2O_2$ product on similar treatment. This compound, homologous with 1-methyl-4-nitromethylenequinolane (VII), was assigned the structure 1,2-dimethyl-4-nitromethylenequinolane (XII) on the basis of analogy of reaction at the open 4-position, similarity of location of the pertinent infrared absorption peaks, and close over-all similarity of the ultraviolet absorption curves (Fig. 2) for $C_{12}H_{12}N_2O_2$ and VII.



XI XII

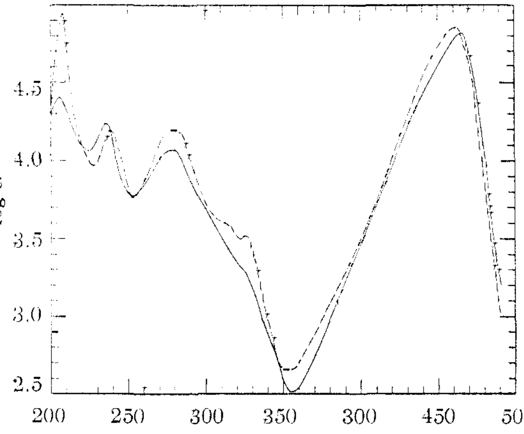


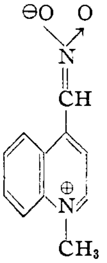
Fig. 2.—Ultraviolet absorption spectra: ——, 1-methyl-4-nitromethylenequinolane; – – –, 1,2-dimethyl-4-nitromethylenequinolane.

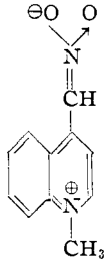
The frequencies of certain infrared absorption peaks exhibited by 1-methyl-4-nitromethylenequinolane (VII), namely, 1630, 1609, 1508 and 1344 cm.$^{-1}$, are similar to those of the main peaks for *o*-hydroxy-β-nitrostyrene (1623, 1606, 1491 and 1337 cm.$^{-1}$, respectively), and these absorption maxima are probably due to the nitro and phenyl groupings similarly constituted in these two molecules. The 200–500 mμ absorption curve for 1-methyl-4-nitromethylenequinolane (Fig. 2) has a maximum of high

---

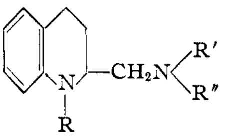
[10] H. Rupe, R. Paltzer and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937).

intensity (log ε 4.82) in the visible region at 466 mμ, indicative of the ready transition of the unusual chromophoric grouping present in VII (also in XII) to probable excited states represented by XIII and XIV. Where such transitions are prevented, as in the hydrobromide of 1-methyl-4-nitromethylenequinolane, the intense absorption in the visible region disappears; *viz.*, the hydrobromide is very pale yellow in contrast to the deep-orange free base. In the ultraviolet region (Fig. 2), 1-methyl-4-nitromethylenequinolane exhibits an inflection point at approximately 326 mμ (1,2-dimethyl-4-nitromethylenequinolane has a definite maximum in the same region),[11] and the series of absorption maxima at 279, 236 and 206 mμ is reminiscent of the series of maxima exhibited by N,N-dimethyl-*o*-toluidine (280,[12] 245[12] and 207 mμ[13]).


XIII


XIV

It has been mentioned previously that we synthesized 1-methyl-2-aminomethyltetrahydroquinoline (X) for comparison with the $C_{11}H_{16}N_2$ diamine derived from the original nitromethane condensation product. There were available for the synthesis of compound X two methods due to Rupe, Paltzer and Engel,[10] one of which involved the methylation of 2-aminomethyltetrahydroquinoline (XV) in methanol solution by means of methyl iodide and potassium hydroxide, whereby X was produced along with the trimethylated product, 1-methyl-2-dimethylaminomethyltetrahydroquinoline (XVIII), and its methiodide. In our hands, application of this same methylation procedure to XV yielded predominantly a dimethylated product, identified as 2-dimethylaminomethyltetrahydroquinoline (XVII), and some hydriodide of the trimethylated compound (XVIII). The proof of structure XVII as correct for the dimethylated product thus obtained incidental to the main investigation was accomplished by the indirect method of synthesizing by unequivocal means the other dimethylation possibility, 1-methyl-2-methylaminomethyltetrahydroquinoline (XVI), and then observing the differences in the properties of the two compounds and their respective derivatives. The monohydrobromide of XVII melted at 187–189°; that of XVI, at 232–233°. The monopicrate of XVII melted at 111–112°; that of XVI, at 153–154°.



	R	R'	R''
XV	H	H	H
X	CH_3	H	H
XVI	CH_3	CH_3	H
XVII	H	CH_3	CH_3
XVIII	CH_3	CH_3	CH_3
XIX	H	Bz	H
XX	CH_3	Bz	H
XXI	CH_3	Bz	CH_3

The synthesis of 1-methyl-2-methylaminomethyltetrahydroquinoline (XVI) was initiated by the 1-methylation of 2-benzoylaminomethyltetrahydroquinoline (XIX). Rupe, Paltzer and Engel[10] did not report a yield for the conversion of XIX to XX by means of methyl iodide in methanol, but by the simple modification of adding sodium bicarbonate to the methylation mixture an 85% yield of 1-methyl-2-benzoylaminomethyltetrahydroquinoline (XX) was obtained. The side-chain N-methylation of the amide XX was accomplished by treating the sodium salt with methyl iodide to give XXI. Hydrolysis of XXI furnished 1-methyl-2-methylaminomethyltetrahydroquinoline (XVI) in satisfactory over-all yield from XX.

The synthesis of 1-methyl-2-dimethylaminomethyltetrahydroquinoline (XVIII) was best accomplished by the methylation of 1-methyl-2-aminomethyltetrahydroquinoline (X) using methyl iodide and sodium bicarbonate, rather than the conditions of Rupe and his co-workers.[11] The precursor X was best prepared by the acid hydrolysis of XX.[10] The trimethylated product XVIII was fully characterized and the methiodide and picrate derivatives were prepared. The hydriodide of XVIII was shown to be the solid product obtained from the methyl iodide and potassium hydroxide methylation of 2-aminomethyltetrahydroquinoline XV, as mentioned above.

Our finding that direct dimethylation of 2-aminomethyltetrahydroquinoline (XV) produced 2-dimethylaminomethyltetrahydroquinoline (XVII) predominantly lends support to the opinion of von Bidder and Rupe[14] that their dialkylation product from XV with ethylene oxide was truly 2-[bis-(β-hydroxyethyl)-aminomethyl]-tetrahydroquinoline rather than the isomeric 1-β-hydroxyethyl-2-β-hydroxyethylaminomethyltetrahydroquinoline.

In conclusion, it should be pointed out that the formation of 1-methyl-4-nitromethylenequinolane (VII) by condensation of 1-methylquinolinium iodide with nitromethane in the presence of base is closely analogous to the preparation of cyanine dyes[15] from 1-alkylquinolinium and 1-alkyllepidinium iodides in the presence of base and isocyanine dyes[16] from 1-alkylquinolinium and 1-alkylquinaldinium iodides in the presence of base. The production of these and related dyes likewise depends upon combination of the active methyl compound with the quinolinium compound at the 4-position, with attendant dehydrogenation to produce the exocyclic double bond at C_4. The reaction of quinolinium compounds with simpler active methyl (and

---

[11] For comparison, the absorbing system present in 1,4-naphthoquinone and its 2-alkyl derivatives shows an absorption maximum at about 334 mμ and a marked inflection in the 390–460 mμ region (R. A. Morton, "The Application of Absorption Spectra to the Study of Vitamins, Hormones and Coenzymes," Adam Hilger, Ltd., London, England, second edition, 1942, pp. 124, 125).

[12] W. R. Remington, THIS JOURNAL, **67**, 1838 (1945).

[13] H. B. Klevens and J. R. Platt, *ibid.*, **71**, 1714 (1949).

[14] H. von Bidder and H. Rupe, *Helv. Chim. Acta*, **22**, 1269 (1939).

[15] *E.g.*: S. Hoogewerff and W. A. VanDorp, *Rec. trav. chim.*, **2**, 317 (1883); A. Miethe and G. Book, *Ber.*, **37**, 2821 (1904).

[16] *E.g.*: S. Hoogewerff and W. A. VanDorp, *Rec. trav. chim.*, **3**, 337 (1884); A. Kaufmann and E. Vonderwahl, *Ber.*, **45**, 1404 (1912); A. Miethe and G. Book, *ibid.*, **37**, 2008 (1904).

methylene) compounds has apparently been hitherto unexplored, and the present findings with nitromethane indicate the desirability of extending the study to determine the scope of this condensation–dehydrogenation process.

Experimental[17]

Absorption Spectra.—The infrared absorption spectra reported in this paper were obtained for each compound in Nujol suspension using a Perkin–Elmer Infrared Spectrometer, Model 12B. The ultraviolet absorption spectra were determined in 95% ethanol solution using a Cary Recording Spectrophotometer, Model 11.

1-Methyl-4-nitromethylenequinolane (VII).—Numerous variations in the quantities of reactants and their mode of addition, in the solvent employed, and in the oxidizing agent (if any) added led to the conditions given below as optimum for the preparation of VII. A nitrogen atmosphere was employed in order to provide for a more controlled oxidation, but it is not considered necessary. A solution of 18.3 g. (0.30 mole) of nitromethane in 100 ml. of absolute ethanol was added slowly with stirring and cooling to a solution of 6.7 g. (0.30 atom) of sodium in 200 ml. of absolute ethanol maintained under nitrogen. A solution of 81.3 g. (0.30 mole) of 1-methylquinolinium iodide, m.p. 133°, in 800 ml. of absolute ethanol was then added slowly. The reaction mixture was heated on the steam-bath for three hours after the addition of 36.9 g. of redistilled nitrobenzene. The orange needles which separated on cooling the final reaction mixture were removed by filtration and recrystallized twice from methanol, m.p. 204° (dec.); yield 22.1 g. (36%).

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.99; N, 13.85. Found: C, 65.22; H, 5.07; N, 14.13.

The picrate, made by combination of equivalent quantities of the aminonitro compound and picric acid in ethanol, was recrystallized from absolute ethanol; yellow prisms, m.p. 135°.

Anal. Calcd. for $C_{17}H_{13}N_5O_9$: C, 47.34; H, 3.04; N, 16.24. Found: C, 47.17; H, 3.28; N, 16.43.

The hydrobromide was formed by heating a mixture of 9.37 g. (0.046 mole) of 1-methyl-4-nitromethylenequinolane in 50 ml. of ethanol with 7.80 g. of 48% hydrobromic acid (0.046 mole) until solution was complete. The solid which separated on cooling was recrystallized from 95% ethanol; pale yellow needles, m.p. 156° (dec.); yield 12.1 g. (92%).

Anal. Calcd. for $C_{11}H_{11}BrN_2O_2$: C, 46.66; H, 3.92; N, 9.90. Found: C, 46.50; H, 4.13; N, 10.13.

Reduction of 1-Methyl-4-nitromethylenequinolane. 1-Methyl-4-aminomethyltetrahydroquinoline (IX).—A solution of 12.1 g. (0.043 mole) of 1-methyl-4-nitromethylenequinolane hydrobromide in 100 ml. of 95% ethanol was hydrogenated at 25° and 3–4 atmospheres using 6 g. of Raney nickel. After four moles of hydrogen had been absorbed, the catalyst was removed by filtration. The filtrate was acidified with dilute hydrochloric acid, and the acidic solution was concentrated *in vacuo*. Treatment of the residue with excess 20% sodium hydroxide was followed by ether extraction. The combined ether extracts were dried and the ether was removed. Distillation of the residue gave 5.50 g. (74%) of a nearly colorless liquid, b.p. 110° (0.4 mm.), $n^{20}D$ 1.5850, which had the correct analysis for 1-methyl-4-aminomethyltetrahydroquinoline.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15. Found: C, 74.76; H, 9.37.

1-Methyl-4-benzoylaminomethyltetrahydroquinoline.—The benzoyl derivative of IX, made in the usual manner, crystallized from ethyl acetate as colorless plates, m.p. 143–144°.

Anal. Calcd. for $C_{18}H_{20}N_2O$: C, 77.09; H, 7.20; N, 10.00. Found: C, 76.86; H, 7.26; N, 10.13.

Reduction of 1-Methyl-4-cyanoquinolinium Iodide. 1-Methyl-4-aminomethyltetrahydroquinoline.—A solution of 14.95 g. (0.05 mole) of 1-methyl-4-cyanoquinolinium iodide,[7a] m.p. 217° (dec.), in 125 ml. of 70% ethanol was hydrogenated at 25° and 3–4 atmospheres using 0.1 g. of platinum oxide catalyst. Four moles of hydrogen were absorbed in 12 hours. The catalyst was removed by filtration, and the filtrate, after acidification with dilute hydrochloric acid, was concentrated *in vacuo*. The product was worked up in the same way as that described above. Distillation through an eight-inch helices-packed column gave 3.65 g. (43%) of 1-methyl-4-aminomethyltetrahydroquinoline, b.p. 111° (0.4 mm.), $n^{20}D$ 1.5849. **The benzoyl** derivative, colorless plates of m.p. 143–144° from ethyl acetate, did not depress the melting point of the benzoyl derivative described in the preceding paragraph, and the infrared absorption spectra of the two were identical (see Fig. 1).

1-Methyl-2-benzoylaminomethyltetrahydroquinoline (XX).—The method of Rupe and his co-workers[10,18] was employed for the methylation of 2-benzoylaminomethyltetrahydroquinoline (XIX) with the exception that one mole of sodium bicarbonate was present in the reaction mixture for every mole of XIX and two moles of methyl iodide. Recrystallization of the crude product from absolute ethanol gave 23.9 g. (85%) of 1-methyl-2-benzoylaminomethyltetrahydroquinoline, m.p. 135–136°.

1,2-Dimethyl-4-nitromethylenequinolane (XII).—A solution of 28.5 g. (0.10 mole) of 1-methylquinaldinium iodide, m.p. 192°, and 12.2 g. (0.20 mole) of freshly distilled nitromethane in 400 ml. of methanol maintained under nitrogen was treated with a solution of 250 ml. of 50% methanol containing 6.7 g. of 85% potassium hydroxide (0.10 mole). The reaction mixture was stirred five hours, then neutralized with 50% aqueous acetic acid. The orange needles which separated on cooling the solution were recrystallized twice from nitromethane, then twice from methanol, m.p. 184.5° (dec.); yield 4.25 g. (40%).

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.60; N, 12.99. Found: C, 66.69; H, 5.66; N, 13.13.

When the same conditions were used with 1-methyllepidinium iodide, m.p. 174–175°, the reaction mixture became dark red, and it was impossible to isolate any crystalline aminonitro product.

2-Dimethylaminomethyltetrahydroquinoline (XVII).—A solution of 65.0 g. (0.4 mole) of 2-aminomethyltetrahydroquinoline[10,14,18] (b.p. 167–169° (14 mm.), $n^{20}D$ 1.5985) and 79.3 g. of 85% potassium hydroxide (1.2 moles) in 600 ml. of methanol was cooled, and to this was added 171 g. (1.2 moles) of methyl iodide. After the spontaneous reaction had subsided, the mixture was refluxed for eight hours under an efficient condenser. Concentration of the mixture followed by cooling gave 165 g. of potassium iodide. The filtrate was evaporated under reduced pressure, and treatment of the residual oil and solid with water yielded 3.7 g. of colorless insoluble organic material. Recrystallization from aqueous ethanol raised the melting point of the colorless prisms to 198.5–200°.

Anal. Calcd. for $C_{13}H_{21}IN_2$: C, 46.99; H, 6.37; N, 8.43. Found: C, 47.17; H, 6.52; N, 8.31.

The composition was suggestive of **1-methyl-2-dimethylaminomethyltetrahydroquinoline (XVIII) hydriodide**, and the identity of this salt was established by its direct conversion to the picrate of 1-methyl-2-dimethylaminomethyltetrahydroquinoline (see below).

The water–oil mixture obtained after removal of the hydriodide was extracted with three 100-ml. portions of ether. The ethereal solution was dried, the ether was removed and the residue was fractionally distilled *in vacuo*, yielding 29.2 (38.4%) of **2-dimethylaminomethyltetrahydroquinoline**, b.p. 93–95.2° (0.18–0.30 mm.), $n^{20}D$ 1.5632, and starting material, $n^{20}D$ 1.5985.

Anal. Calcd. for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.72. Found: C, 75.53; H, 9.66; N, 14.91.

The monohydrobromide of XVII was prepared by adding the theoretical amount of 48% hydrobromic acid to an ethanol solution of the amine and then adding ether. Recrystallization from 95% ethanol gave colorless prisms, m.p. 187–189°.

Anal. Calcd. for $C_{12}H_{19}BrN_2$: C, 53.14; H, 7.06; N, 10.33. Found: C, 53.20; H, 7.15; N, 10.27.

The picrate of XVII was formed in ethanol from equimolar portions of the amine and picric acid and was recrys-

---

[17] All melting points are corrected. The authors are indebted to Miss Elizabeth M. Petersen for determination of the infrared absorption spectra and to Miss Ella L. Richards for determination of the ultraviolet absorption spectra.

[18] A. Gassmann and H. Rupe, *Helv. Chim. Acta*, **22**, 1241 (1939).

tallized from 95% ethanol; orange prisms, m.p. 111–112° after sintering at 110°.

Anal. Calcd. for $C_{18}H_{21}N_5O_7$: C, 51.55; H, 5.05; N, 16.70. Found: C, 51.73; H, 5.20; N, 16.58.

1-Methyl-2-methylaminomethyltetrahydroquinoline (XVI).—The general procedure for the N-alkylation of the amide of a primary amine was employed.[19] A mixture of 10.23 g. (0.04 mole) of 1-methyl-2-benzoylaminomethyltetrahydroquinoline (XX) and 150 ml. of xylene was distilled until the distillate was no longer cloudy. To the cooled mixture was added 1.15 g. (0.05 atom) of sodium, and the resulting mixture was heated at about 140° for three hours. Following cooling, 7.10 g. (0.05 mole) of methyl iodide was added, and the mixture was heated at 80° for 12 hours. Excess methyl iodide and xylene were removed by distillation at reduced pressure, and 10 ml. of 95% ethanol was added to remove any unreacted sodium. After the addition of 30 ml. of concentrated hydrochloric acid, the aqueous mixture was refluxed for 48 hours. The benzoic acid which separated upon cooling was removed by filtration, and the filtrate was made strongly alkaline with concentrated sodium hydroxide. Ether extraction followed by drying and removal of the ether gave a liquid which was fractionally distilled *in vacuo;* yield 3.88 g. (51% over-all) of **1-methyl-2-methylaminomethyltetrahydroquinoline**, b.p. 134° (8 mm.), $n^{20}D$ 1.5680, and 1.55 g. of 1-methyl-2-aminomethyltetrahydroquinoline (X), b.p. 148° (8 mm.), $n^{20}D$ 1.5943 (by hydrolysis of unreacted amide).

Anal. Calcd. for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.73. Found: C, 75.87; H, 9.55; N, 14.52.

The **monohydrobromide** of XVI crystallized as prisms from 95% ethanol, m.p. 232–233°.

Anal. Calcd. for $C_{12}H_{19}BrN_2$: C, 53.14; H, 7.06; N, 10.33. Found: C, 52.89; H, 7.24; N, 10.60.

The **monopicrate** of XVI was formed in and recrystallized from ethanol; red elongated prisms, m.p. 153–154°.

Anal. Calcd. for $C_{18}H_{21}N_5O_7$: C, 51.55; H, 5.05; N, 16.70. Found: C, 51.78; H, 5.19; N, 16.61.

1-Methyl-2-dimethylaminomethyltetrahydroquinoline (XVIII).—To a cooled solution of 9.74 g. (0.055 mole) of 1-methyl-2-aminomethyltetrahydroquinoline (X)[10,18] (b.p. 137° (2 mm.), $n^{20}D$ 1.5945) in 50 ml. of absolute methanol were added 9.30 g. (0.111 mole) of sodium bicarbonate and 15.70 g. (0.111 mole) of methyl iodide in 50 ml. of methanol. The reaction mixture was refluxed for twelve hours, cooled, and the insoluble crystalline material was removed by filtration. The filtrate was further concentrated *in vacuo*, and the resulting oil and crystal mixture was treated with three 50-ml. portions of ether. The ether extracts were combined and dried, and the ether was removed. Distillation of the residue through an eight-inch helices-packed column gave two fractions: 4.65 g. (65% yield based on unrecovered starting material) of **1-methyl-2-dimethylaminomethyltetrahydroquinoline**, b.p. 109–110° (0.5 mm.), $n^{20}D$ 1.5775, and 3.50 g. of starting material (X), b.p. 119–120° (0.5 mm.), $n^{20}D$ 1.5945.

Anal. Calcd. for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.45; H, 9.83; N, 13.92.

The crystalline materials isolated in the procedure described above were combined and treated with 50 ml. of cold water to remove the sodium iodide. The water-insoluble residue was recrystallized from 95% ethanol to give 3.50 g. of the **methiodide** of 1-methyl-2-dimethylaminomethyltetrahydroquinoline (XVIII) as colorless plates, m.p. 191–192°. The melting point reported by Rupe, Paltzer and Engel[10] was 204°.

Anal. Calcd. for $C_{14}H_{23}IN_2$: C, 48.56; H, 6.69; N, 8.09. Found: C, 49.02; H, 6.91; N, 7.98.

The **monopicrate** of XVIII was made from equimolar quantities of the amine (XVIII) and picric acid. Three recrystallizations from ethanol gave orange-red prisms, m.p. 164–165°. By contrast, Rupe, Paltzer and Engel[10] reported a melting point of 122° for 1-methyl-2-dimethylaminomethyltetrahydroquinoline picrate.

Anal. Calcd. for $C_{19}H_{23}N_5O_7$: C, 52.53; H, 5.57; N, 16.12. Found: C, 52.44; H, 5.37; N, 16.17.

When the hydriodide, m.p. 198.5–200°, obtained from the treatment of XV with methyl iodide in the presence of potassium hydroxide (see above) was treated with an excess of picric acid in ethanol, orange-red prisms, m.p. 164–165°, of monopicrate were isolated.

Anal. Calcd. for $C_{19}H_{23}N_5O_7$: C, 52.53; H, 5.57; N, 16.12. Found: C, 52.57; H, 5.42; N, 16.06.

This picrate sample, when mixed with the picrate made directly from the amine XVIII, gave no depression in melting point.

URBANA, ILL. RECEIVED JANUARY 8, 1951

---

[19] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, London, England, 1948, second edition, p. 300.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY AND THE AMERICAN PETROLEUM INSTITUTE RESEARCH PROJECT 45]

The Quantitative Inversion of *cis*- and *trans*-Alkene Isomers: A New Synthesis of Normal *cis*-Alkenes[1]

BY MELVERN C. HOFF,[2] KENNETH W. GREENLEE AND CECIL E. BOORD

A new method is described for quantitatively inverting the configuration about the carbon to carbon double bond in *n*-alkenes, involving molecular chlorination (*trans*), alkaline dehydrochlorination (*trans*), and dechlorination (without change in configuration) by sodium in ammonia. The method was applied to the *trans*-isomers of 2-pentene, 2-hexene, 3-hexene, 2-octene and 4-octene and the *cis*-isomer of 3-hexene. Quantitative data are given for the stereospecificity of the reactions, and the corresponding reaction mechanisms are discussed. Physical properties are given for five *cis*-alkenes which were prepared in higher purity than previously reported.

To further a program for the preparation of hydrocarbons[3] it was desired to develop a method for the production of normal *cis*-alkenes suitable for use in the preparation of standard samples[4] and for engine testing.[5] Fairly high purity of the product and ease of further purification were therefore of primary importance. Although *cis*-*n*-alkenes are readily produced by catalytic hydrogenation of the corresponding alkynes,[6,7] cryoscopic examination of the *cis* isomers produced in this manner has shown them not to be of high

---

[1] The material in this paper was abstracted from the dissertation submitted by Melvern C. Hoff to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in 1948. Part of it was presented before the Organic Division at the 115th Meeting of the American Chemical Society, San Francisco, March, 1949.

[2] Standard Oil Company of Indiana, Whiting, Indiana.

[3] The American Petroleum Institute Research Project 45, for the "Synthesis and Properties of Hydrocarbons of Low Molecular Weight," administered by The Ohio State University Research Foundation.

[4] Demmerle, *Chem. Eng. News*, **24**, 2020 (1946).

[5] Lovell, *Ind. Eng. Chem.*, **40**, 2388 (1948).

[6] Campbell and O'Connor, THIS JOURNAL, **61**, 2897 (1939).

[7] Campbell and Eby, *ibid.*, **63**, 216, 2683 (1941).